

Controlling the Dynamics of Many-Electron Systems from First Principles: A Marriage of Optimal Control and Time-Dependent Density-Functional Theory

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Abstract

Quantum Optimal Control Theory (QOCT) provides the necessary tools to theoretically design driving fields capable of controlling a quantum system towards a given state or along a prescribed path in Hilbert space. This theory must be complemented with a suitable model for describing the dynamics of the quantum system. Here, we are concerned with many electron systems (atoms, molecules, quantum dots, etc) irradiated with laser pulses. The full solution of the many electron Schrödinger equation is not feasible in general, and therefore, if we aim to an *ab initio* description, a suitable choice is time-dependent density-functional theory (TDDFT). In this work, we establish the equations that combine TDDFT with QOCT, and demonstrate their numerical feasibility with examples.

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The quest for systems able to perform quantum computing [1], the synthesis of design-molecules by laser-induced chemical reactions [2], or the control of electron currents in molecular switches using light [3] may benefit from the recent advances in the field of design and synthesis of laser pulses specially tailored to perform a specific task [4]. The laser pulse creation and shaping techniques have improved impressively over the last decades, and thus the area of experimental optimal control has become a well established field.

Such pulses can also be theoretically derived with the help of quantum optimal control theory [5–7] (QOCT). This theory is rather general in scope, and its basic formulation makes no assumption on the nature and modelling of the quantum system on which the pulse is applied. In practice, the solution of the QOCT equations requires multiple propagations, both forwards and backwards, for the system under study. Since these propagations are in general unfeasible for many-particle systems, few-level simplifications and models are typically postulated when handling the QOCT equations. Unfortunately, these simplifications are not always accurate enough: strong pulses naturally involve many levels, and normally perturbative treatments are not useful. Non linear laser-matter interaction must sometimes be described *ab initio*.

In this work, we are concerned with many-electrons systems (atoms, molecules, quantum dots...) irradiated with femtosecond (or attosecond) pulses, with intensities typically ranging from 10^{11} to 10^{15} Wcm $^{-2}$ (a non-linear regime that nevertheless allows for a non-relativistic treatment). This may lead to a number of interesting phenomena, e.g. above-threshold or tunnel ionization, bond hardening or softening, high harmonic generation, photo-isomerization, photo-fragmentation, Coulomb explosion, etc [8]. In order to describe this type of processes from first principles, time-dependent density-functional theory [9] (TDDFT) has emerged as a viable alternative to more computationally expensive approaches based on the wave function.

In TDDFT, the system of interacting electrons is substituted by a proxy system of non-interacting electrons – the “Kohn-Sham” (KS) system, which is computationally much less demanding. The theory guarantees the identity of the electronic densities of the two systems, and the existence of a density functional for each possible observable, thus allowing (in principle) the computation of any property without ever dealing with the many-body wave function. The theory is however hindered by the lack of knowledge of the precise external potential seen by the auxiliary non-interacting system (the so-called “exchange and correlation” potential, which is a functional of the density itself, has to be approximated), and, in many cases, the precise form of the density functional that provides the required observable. Fortunately, a number of valid approximations

for these density functionals have been developed over the years, which have made of TDDFT a computationally efficient possibility to describe many processes.

We are thus led to the necessity of inscribing TDDFT into the general QOCT framework. We will lay down and discuss the equations that result when TDDFT is used to model the system. Then, in order to demonstrate the computational feasibility, we present one sample calculation: a 2D two-electron system being optimally driven between two potential wells.

In the spirit of TDDFT, we substitute the problem of formulating QOCT in terms of the real interacting system, by the formulation of the optimization problem for the non-interacting system of electrons. The equations of motion for the single-particle orbitals of this system, also known as time-dependent KS (TDKS) equations, are:

$$\begin{aligned} i\frac{\partial\varphi_i}{\partial t}(\vec{r}\sigma,t) &= \langle\vec{r}\sigma|\hat{H}_{\text{KS}}[n_{\tau\omega}(t),u,t]|\varphi_i(t)\rangle = \\ &= -\frac{1}{2}\nabla^2\varphi_i(\vec{r}\sigma,t) + \langle\vec{r}\sigma|\hat{V}_0|\varphi_i(t)\rangle + v_H[n(t)](\vec{r})\varphi_i(\vec{r}\sigma,t) + \\ &+ \langle\vec{r}\sigma|\hat{V}_{\text{xc}}[n_{\tau\omega}(t)]|\varphi_i(t)\rangle + \langle\vec{r}\sigma|\hat{V}_{\text{ext}}[u]|\varphi_i(t)\rangle, \end{aligned} \quad (1)$$

$$n_{\tau\omega}(\vec{r},t) = \sum_{i=1}^N \varphi_i^*(\vec{r}\tau,t)\varphi_i(\vec{r}\omega,t), \quad (2)$$

$$n(\vec{r},t) = \sum_{\sigma} n_{\sigma\sigma}(\vec{r},t), \quad (3)$$

for $i = 1, \dots, N$ orbitals. The greek indexes $\sigma, \tau, \omega \dots$ run over the two spin configurations, up and down. The densities are, by construction, equal to that of the *real*, interacting system of electrons. \hat{V}_0 represents the internal, time independent fields – usually a nuclear Coulomb potential $V_n(\vec{r})$, and may include as well a spin-orbit coupling term of the form $\vec{\sigma} \cdot \vec{\nabla} V_n \times \hat{p}$ (where $\vec{\sigma}$ is the vector of Pauli matrices). The term $v_H[n(t)](\vec{r}) = \int d^3r' \frac{n(\vec{r}',t)}{|\vec{r}-\vec{r}'|}$ is the Hartree potential, and $\hat{V}_{\text{xc}}[n_{\tau\omega}]$ is the exchange and correlation potential operator, whose action is given by:

$$\langle\vec{r}\sigma|\hat{V}_{\text{xc}}[n_{\tau\omega}(t)]|\varphi_i(t)\rangle = \sum_{\beta} v_{\text{xc}}^{\sigma\beta}[n_{\tau\omega}(t)](\vec{r})\varphi_i(\vec{r}\beta,t). \quad (4)$$

Note that, for the sake of generality, we allow a spin-resolved exchange and correlation potential, that depends on the four spin components $n_{\tau\delta}$ (in many situations more restricted dependences are assumed). However, we do assume here an *adiabatic* approximation, i.e. v_{xc} at each time t is a functional of the densities at that time, $n_{\tau\omega}(t)$. This restriction is non-essential for the derivations that follow, but the use of non-adiabatic functionals is very scarce, and adiabatic approximations will result in simpler equations.

The last potential term, \hat{V}_{ext} , is the external time-dependent potential, which is determined by a “control” u . In a typical case, this external potential is the electric pulse created by a laser source in the dipole approximation, and u is the real time-dependent function that determines its temporal shape (in this case, $\langle \vec{r}\sigma | \hat{V}_{\text{ext}}[u] | \varphi_i(t) \rangle = u(t) \vec{r} \cdot \vec{p} \varphi_i(\vec{r}\sigma, t)$, where \hat{p} is the polarization vector of the pulse). We write it however in general operator form, since it can be a 2x2 matrix which may include both a time-dependent electric field as well as a Zeeman-coupled magnetic field [10]. The mathematical nature of u may also be diverse: it may not be a time-dependent function, but a set of N parameters that determine the precise form of the electric field.

If we group the N single particle states into a vector $\underline{\varphi}(t)$, we can rewrite the TDKS equations in a matrix form:

$$i\dot{\underline{\varphi}}(t) = \underline{\hat{H}}[n_{\tau\omega}(t), u, t] \underline{\varphi}(t), \quad (5)$$

where $\underline{\hat{H}}[n_{\tau\omega}(t), u, t] = \hat{H}_{\text{KS}}[n_{\tau\omega}(t), u, t] \underline{I}_N$ and \underline{I}_N is the N -dimensional unit matrix. With this notation we stress the fact that we have only *one* dynamical system – and not N independent ones, since all φ_i are coupled. This coupling, however, comes solely through the density, since the Hamilton matrix is diagonal.

The specification of the value of the control u , together with the initial conditions, determines the solution orbitals: $u \rightarrow \underline{\varphi}[u]$. Our task is now the following: we wish to find an external field – in the language of OCT, a control u – that induces some given behaviour of the system, which can be mathematically formulated by stating that the induced dynamics maximizes some target functional F . Since we are using TDDFT, this functional will be defined in terms of the KS orbitals, and will possibly depend explicitly on the control u :

$$F = F[\underline{\varphi}, u]. \quad (6)$$

Since the KS orbitals depend on u as well, the goal of QOCT can be formulated as finding the maximum of the function:

$$G[u] = F[\underline{\varphi}[u], u]. \quad (7)$$

In the most general case, the functional F depends on $\underline{\varphi}$ at all times during the process (we have a “time-dependent target”). In many cases, however, the goal is the achievement of some target at a given time T that determines the end of the propagation interval (we then have a “static target”). In both cases, the determination of the value of the function G is obtained by performing the propagation of the system with the field determined by the control u .

There are many optimization algorithms capable of maximizing functions utilizing solely the knowledge of the function values (“gradient-free algorithms”). We have recently employed one of them in this context [11]. However, QOCT provides the solution to the problem of computing the gradient of G – or, properly speaking, the functional derivative if u is a function. The non-linear dependence of the Hamiltonian with the density slightly complicates the derivation, but we sketch the key steps: First, we must note that searching for a maximum of G is equivalent to a constrained search for F – constrained by the fact that the $\underline{\phi}$ orbitals must fulfill the TDKS equations. In order to do so, we introduce a new set of orbitals $\underline{\chi}$ that act as Lagrange multipliers, and define a new functional J by adding a Lagrangian term L to F :

$$J[\underline{\phi}, \underline{\chi}, u] = F[\underline{\phi}, u] + L[\underline{\phi}, \underline{\chi}, u], \quad (8)$$

$$L[\underline{\phi}, \underline{\chi}, u] = -2 \sum_{j=1}^N \text{Re} \left[\int_0^T dt \langle \chi_j(t) | i \frac{d}{dt} + \hat{H}_{\text{KS}}[n_{\tau\omega}(t), u, t] | \phi_j(t) \rangle \right]. \quad (9)$$

Setting the functional derivatives of J with respect to the χ orbitals to zero, we retrieve the TDKS equations. In an analogous manner, we obtain a set of solution $\underline{\chi}[u]$ orbitals by taking functional derivatives with respect to $\underline{\phi}$:

$$\frac{\delta J}{\delta \underline{\phi}^*} = 0 \Rightarrow$$

$$i \dot{\underline{\chi}}(t) = \left[\hat{H}_{\text{KS}}[n_{\tau\sigma}[u](t), u, t] + \hat{K}[\underline{\phi}[u](t)] \right] \underline{\chi}(t) - i \frac{\delta F}{\delta \underline{\phi}^*}, \quad (10)$$

$$\underline{\chi}(T) = \underline{0}. \quad (11)$$

The non-diagonal operator matrix $\hat{K}[\underline{\phi}[u](t)]$ is defined by the operators:

$$\langle \vec{r}\sigma | \hat{K}_{ij}[\underline{\phi}[u](t)] | \Psi \rangle = -2i \sum_{\kappa} \phi_i[u](\vec{r}\kappa, t) \times \text{Im} \left[\sum_{\alpha\beta} \int d^3 r' \Psi^*(\vec{r}'\alpha) f_{\text{Hxc}}^{\alpha\beta, \sigma\kappa}[n_{\tau\omega}[u](t)](\vec{r}, \vec{r}') \phi_j[u](\vec{r}'\beta, t) \right], \quad (12)$$

$$f_{\text{Hxc}}^{\alpha\beta, \gamma\delta}[n_{\tau\omega}](\vec{r}, \vec{r}') = \frac{\delta_{\alpha\beta} \delta_{\gamma\delta}}{|\vec{r} - \vec{r}'|} + \frac{\delta v_{\text{xc}}^{\alpha\beta}[n_{\tau\omega}](\vec{r})}{\delta n_{\gamma\delta}(\vec{r}')}. \quad (13)$$

If we now note that $G[u] = J[\underline{\phi}[u], \underline{\phi}[u], u]$, we arrive to:

$$\nabla_u G[u] = \nabla_u F[\underline{\phi}, u] \Big|_{\underline{\phi}=\underline{\phi}[u]} + 2 \text{Im} \left[\sum_{j=1}^N \int_0^T dt \langle \chi_j[u](t) | \nabla_u \hat{V}_{\text{ext}}[u](t) | \phi_j[u](t) \rangle \right] \quad (14)$$

Several aspects of these equations deserve further discussion:

(1) Eqs. 10 and 11 are a set of first-order differential equations, whose solution must be obtained by *backwards* propagation, since the boundary condition, Eq. 11 is given at the end of the propagating interval, T . Note that this propagation depends on the time-dependent KS orbitals $\underline{\varphi}[u]$. Therefore, the numerical procedure to follow consists of a forward propagation to obtain $\underline{\varphi}[u]$, followed by a backwards propagation to obtain $\underline{\chi}[u]$.

(2) These backwards equations are non-homogeneous, due to the presence of the last term in Eq. 10, the functional derivative of F with respect to $\underline{\varphi}$ – but see point (4) below.

(3) Often, the control target functional F is split like:

$$F[\underline{\varphi}, u] = J_1[\underline{\varphi}] + J_2[u]. \quad (15)$$

J_1 codifies the actual purpose of the optimization, whereas J_2 imposes a *penalty* on the control function, in order to avoid, for example, the solution field to have unreasonable amplitudes. In the following, we will assume this division.

(4) The previous equations (10-11) refer to a general “time-dependent target” case, as mentioned above. In many cases of interest, the target functional F takes a “static” form, which can be expressed as:

$$J_1[\underline{\varphi}, u] = O[\underline{\varphi}(T), u], \quad (16)$$

for some functional O whose argument is not the full evolution of the KS system, but only its value at the end of the propagation. In this case, the non-inhomogeneity in Eq. 10 vanishes, and instead we obtain a different final-value condition:

$$\chi_i[u](\vec{r}\sigma, T) = \frac{\delta O[\underline{\varphi}[u], u]}{\delta \varphi_i^*(\vec{r}\sigma)}. \quad (17)$$

(5) The previous Eq. 14 assumes that u is a set of N parameters, $u \in \mathbb{R}^N$ that determines the control function. If u is directly the control function, the gradient has to be substituted by a functional derivative, and the result is:

$$\frac{\delta G}{\delta u(t)} = \left. \frac{\delta F[\underline{\varphi}, u]}{\delta u(t)} \right|_{\underline{\varphi}=\underline{\varphi}[u]} + 2\text{Im} \left[\sum_{j=1}^N \langle \chi_j[u](t) | \hat{D} | \varphi_j[u](t) \rangle \right]. \quad (18)$$

We have assumed here that the external potential \hat{v}_{ext} is determined by the function u by a linear relationship:

$$\hat{V}_{\text{ext}}[u](t) = u(t)\hat{D}. \quad (19)$$

This is the most usual case (\hat{D} would be the dipole operator, and $u(t)$ the amplitude of an electric field), but of course it would be trivial to generalize this to other possibilities.

The previous scheme permits therefore to control the KS system. However, the goal is to control the *real* system. In principle, the target is given by some functional $\tilde{J}_1[\Psi]$ that depends on the *real* many-electron wave function of the interacting system. This object is not provided by TDDFT, that only provides the density n . Therefore, the ideal situation would be that in which \tilde{J}_1 depends on Ψ only through the density n , $\tilde{J}_1 = \tilde{J}_1[n]$. In this manner, optimizing for the KS system is strictly equivalent to optimizing for the real one. For example, this holds if \tilde{J}_1 is given by the expectation value of some one-body local operator \hat{A} :

$$\tilde{J}_1[\Psi] = \langle \Psi(T) | \hat{A} | \Psi(T) \rangle = \int d^3r n(\vec{r}, T) a(\vec{r}), \quad (20)$$

where $\hat{A} = \sum_{i=1}^N a(\hat{r}_i)$. In this case, Eq. 17 is simply:

$$\chi_i[u](\vec{r}\sigma, T) = a(\vec{r}) \phi_i[u](\vec{r}\sigma, T). \quad (21)$$

This will be the kind of target that we will be using in the example below. Note that TDDFT ensures that all observables are functionals of the density, and therefore *in principle* one could always write such functionals (we will provide another example in a forthcoming publication, in which the target is the high harmonic generation spectrum, which is also an explicit functional of the density).

Unfortunately, in some cases we still need to find the explicit density functional dependence in many cases of interest. For example, a very common control goal is the transition from an initial state to a target state. In other words, the control operator \hat{A} is the projection operator onto the target state $\hat{A} = |\Psi_{\text{target}}\rangle \langle \Psi_{\text{target}}|$. We have no exact manner to substitute, in this case, the \tilde{J}_1 functional by a functional J_1 defined in terms of the density, or in terms of the KS determinant. It can be approximated, however, by an expression in the form:

$$J_1[\underline{\varphi}] = |\langle \underline{\varphi}(T) | \sum_I c_I |\varphi^I\rangle|^2, \quad (22)$$

where $\varphi(T)$ is the TDKS determinant at time T , and we compute its overlap with a linear combination of Slater determinants φ^I , weighted with some coefficients c_I . These Slater determinants would be composed of occupied and unoccupied ground state KS orbitals, $\varphi^I = \det[\varphi_1^I, \dots, \varphi_N^I]$. In this case, Eq. 17 takes the form:

$$\chi_i[u](\vec{r}\sigma, T) = \sum_{IJ} \lambda_{IJ}(\vec{r}\sigma) \langle \underline{\varphi}(T) | \varphi^I \rangle \langle \varphi^J | \underline{\varphi}(T) \rangle, \quad (23)$$

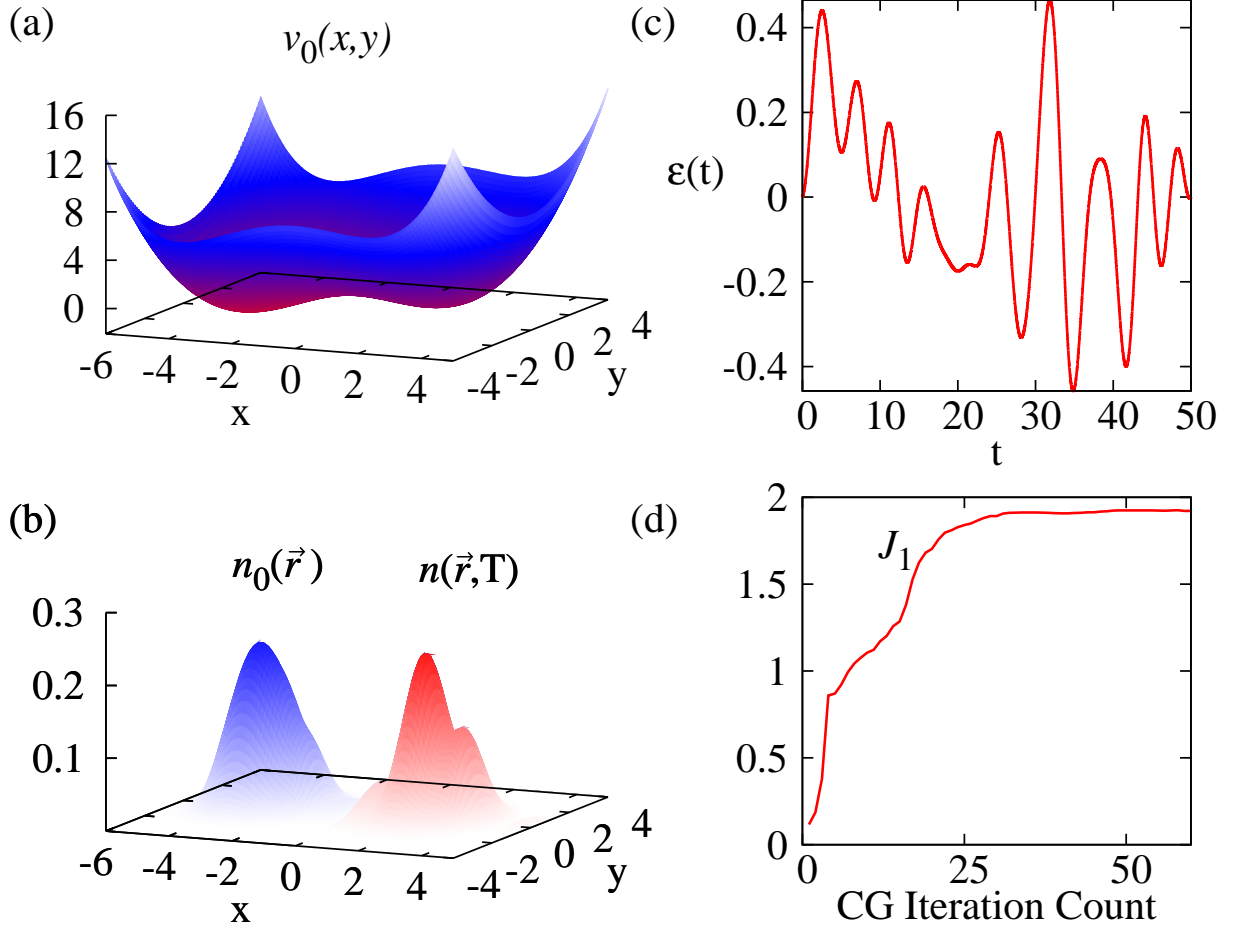


FIG. 1. (a) External potential defining a model for double quantum dot. (b) Density of the initial, ground state (blue) and final, propagated density (red). (c) Optimized electric field for the charge-transfer process described in the text. (d) Convergence history of the conjugate gradient algorithm. All magnitudes are given in effective atomic units.

$$\lambda_{IJ}(\vec{r}\sigma) = c_I c_J^* \text{Tr}\{(\mathbf{M}^I)^{-1} \mathbf{A}_I^i(\vec{r}\sigma)\}, \quad (24)$$

where $\mathbf{M}_{mn}^I = \langle \phi_m | \phi_n^I \rangle$ and $\mathbf{A}_I^i(\vec{r}\sigma)_{mn} = \delta_{mi} \phi_n^I(\vec{r}\sigma)$.

We have implemented the described TDDFT+QOCT formalisms in the octopus code [12]. In the following, we describe a simple example: the charge transfer between two neighboring potential wells, considered as models for 2D quantum dots, such as the ones created in semiconductor heterostructures. We consider a two-electron system, trapped in an asymmetric double quantum dot well modelled by a potential function given by (in the following, we consider effective atomic

units):

$$v_0(x, y) = \frac{1}{64}x^4 - \frac{1}{4}x^2 + \frac{1}{32}x^3 + \frac{1}{2}y^2. \quad (25)$$

The potential landscape is depicted in Fig. 1(a). We then solve the ground state KS equations for this system, by making use of the local density approximation to the exchange and correlation parameterized by Attacalite et al [13]. The ground state density will be localized in the left well (see Fig. 1(b): $n_{\text{gs}}(\vec{r}) = 2|\phi_0^{\text{gs}}(\vec{r})|^2$, where ϕ_0^{gs} is the ground state KS orbital.

We apply an electric field, polarized along the x direction. Its amplitude is parameterized by its Fourier coefficients:

$$\varepsilon(t) = \sum_{n=1}^{M/2} \left[a_n \sqrt{\frac{2}{T}} \cos\left(\frac{2\pi}{T}nt\right) + b_n \sqrt{\frac{2}{T}} \sin\left(\frac{2\pi}{T}nt\right) \right]. \quad (26)$$

The $\{a_n, b_n\}$ coefficients are therefore the control u (although the constraint $\sum_{n=1}^{N/2} a_n = 0$ is enforced in order to ensure $\varepsilon(0) = \varepsilon(T) = 0$). Since our goal is to transfer as much charge as possible from the left to the right well, we formulate a target in the form:

$$F[\underline{\phi}; a, b] = \int_{x>0} d^3r n(\vec{r}, T) - \alpha \sum_{n=1}^{M/2} (a_n^2 + b_n^2). \quad (27)$$

In words, we wish to arrive to a state in which all the density is localized in the $x > 0$ region. The last term of Eq. 27 corresponds to the penalty:

$$J_2[a, b] = -\alpha \int_0^T dt \varepsilon^2(t) = -\alpha \sum_{n=1}^{M/2} (a_n^2 + b_n^2), \quad (28)$$

and it is introduced in order to prevent the solution field from having too much intensity.

The solution field is shown in Fig. 1(c). We have employed a standard conjugate gradients (CG) algorithm to perform the optimization. After around 60 CG iterations [14], the control field is converged and we achieve a value of 1.92 for J_1 – the maximum is 2 (see convergence plot in Fig. 1).

In conclusion, we have shown how TDDFT can be combined with QOCT, and we have demonstrated how the resulting equations are numerically tractable. This provides a scheme to perform QOCT calculations from first principles, in order to obtain tailored function-specific laser pulses capable of controlling the electronic state of atoms, molecules, or quantum dots. Most of the previous applications of QOCT were targeted to control, with femto-second pulses, the motion of the nuclear wave packet on one or few potential energy surfaces, which typically happens on a time scale of hundreds of femtoseconds or picoseconds. The approach developed in this Letter,

on the other hand, is particularly suited to control the motion of the electronic degrees of freedom which is governed by the sub-femto-second time scale. The possibilities that are open thanks to this technique are numerous: shaping of the high harmonic generation spectrum (i.e. quenching or increasing given harmonic orders), selective excitation of electronic excited states that are otherwise difficult to reach with conventional pulses, control of the electronic current in molecular junctions, etc. Work along these lines is in progress.

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